



VANISHING SCHOTTKY BARRIERS IN DIAMOND/METAL INTERFACES

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We present theoretical evidence that Schottky-barrier heights may, for certain types of interfaces, be far more sensitive to interface geometry than previously suspected. We have identified two classes of diamond/metal interface orientations, one of which leads to Schottky-barrier heights of order 1 eV, the other to barrier heights that are very small or zero. This striking difference can be traced to details of the gap-state band structure that arise from different bonding mechanisms, for which the precise atomic geometry plays a crucial role.

Virtually all existing theoretical models of Schottky-barrier formation perforce neglect the precise arrangement of atoms near the interface. This is due in part to experimental necessity, and in part to the desire for a predictive theory based solely on bulk properties, for which the detailed interface geometry is relatively unimportant. Recently, however, it has been shown experimentally that for clean, ordered, epitaxial interfaces, variations in interface geometry can result in variations in the Schottky-barrier height (SBH) of 20-30%. For $\text{NiSi}_2/\text{Si}(111)$, two different interface structures give rise to SBH's of 0.79 and 0.65 eV [1], while for $\text{Pb}/\text{Si}(111)$, two types of interface orientation produce SBH's of 0.92 and 0.70 eV [2]. In this Letter, we describe theoretical evidence for a much more striking sensitivity of the SBH to interface geometry. In particular, for diamond/ $M(111)$ and (100) interfaces ($M=\text{Ni}, \text{Cu}, \text{Al}$), we find that one class of interface orientations leads to SBH's of order 1 eV, and that another class *strongly suppresses* the barrier, and hence leads to ohmic contacts.

High-quality, epitaxial diamond films are now routinely grown by chemical vapor deposition (CVD) on diamond and boron nitride substrates, and polycrystalline films have been grown by several methods on a variety of other substrates [3]. Several groups have attempted diamond-film growth on transition-metal substrates. The most promising such substrates are Cu and Ni; both are well lattice-matched to bulk diamond, and neither forms any stable binary phases with carbon at the temperatures typically used in the CVD process. The diamond/Ni system has been the subject of several recent experimental efforts [4,5], none of which has been successful in growing a clean epitaxial interface.

One of the most elusive requirements for diamond-film growth on metal substrates is to prevent the initial carbon layers from forming graphitic structures. One alternative is to reverse the process, and grow the metal epitaxially on a crystalline diamond substrate [6]. Since clean diamond surfaces are known to reconstruct unless passivated (typically by hydrogen), it is not yet clear what kind of interfaces can be grown this way. However, in light of recent successes in the controlled growth of nearly ideal, epitaxial Si/metal interfaces [1], we believe that theoretical studies of ideal diamond/metal interfaces are well justified.

We have considered two classes of interface orientation (relative positioning of atomic layers at the interface), "tetrahedral" and "in-hollow". Both refer to the orientation parallel to the interface plane; for each orientation, the atoms are fixed at their bulk positions, then the C-M layer separation is varied to minimize the total energy. Tetrahedral orientations are defined by placing the first layer of metal atoms in the positions that would have been occupied by carbon atoms, had the diamond lattice been continued. In this way, the coordination of surface carbon atoms is kept (approximately) tetrahedral. For the (111) and (100) interfaces, the resulting positions are known as the "atop" and "bridge" sites, respectively. For the in-hollow orientations, first-layer metal atoms are placed above the diamond-surface hollows of highest available symmetry. For the (111) and (100) , the resulting positions are known as the "T4" and "4-fold" sites, respectively. In all cases, the remaining layers of metal are placed according to their ideal fcc positions.

Our discussion will focus on interfaces of diamond with fcc Ni, for which the lattice mismatch is less than 1.5%; qualitatively identical results were obtained for Cu (1% mismatch) and Al (large mismatch, but included as a prototype *sp* metal). The Ni and Cu lattice-mismatches are the smallest of the elemental metals; we have performed all calculations using the experimental diamond lattice constant of $a=3.57$ Å (within 1% of the theoretical value) to simulate a strained metal overlayer on a diamond substrate. The interfaces are taken to be ideal: atomically abrupt and with a 1×1 surface unit cell. The local-density approximation (LDA) to density-functional theory is used; the suitability of this approach, for both band offsets [7] and SBH's [8], has been discussed elsewhere. LDA band offsets are generally accurate to 0.1 eV [7]; while less is known regarding the accuracy of SBH's, differences in SBH's for different geometries seem to be at least as accurate [9]. We simulate the isolated interface by a supercell, with slabs consisting of eight layers of diamond alternating with five layers of nickel. The linearized augmented-plane-wave (LAPW) method [10] was used with the Hedin-Lundqvist exchange-correlation potential. Brillouin-zone (BZ) sampling used 28 special k-points in the fcc irreducible BZ, projected on to the surface-BZ appropriate to the interface. Angular momentum expansions of the potential and density were retained up

through $L=6$. Numerical tests demonstrate that our SBH's and total energies are converged to within 0.1 eV, with respect both to basis set and the isolated interface. Further details of the method [11] and preliminary results [12,13,14] have been presented elsewhere.

Since diamond is almost always made semiconducting by boron-doping, we report here the calculated SBH's for p -type semiconductors:

$$\Phi_B = E_F - E_v, \quad (1)$$

where E_F is the Fermi level and E_v is the diamond valence-band (VB) maximum far from the interface. In the LDA, E_F is determined self-consistently; although E_v can in principle be located from the projected density-of-states, we use a simpler prescription that is not prone to ambiguities in the projection algorithm. Since the calculations include all core states, the carbon 1s level near the center of the slab can be aligned with the same level from a separate bulk-diamond calculation. These interior core levels are efficiently shielded from the interface, and so one is justified in setting the energy differences ($E_v - E_{1s}$) for the slab and bulk geometries equal. This determines E_v for the diamond slab, and hence determines Φ_B uniquely and without reference to the density-of-states.

Theoretical total energies and SBH's for diamond/Ni(111) and (100) in the tetrahedral and in-hollow orientations are shown in Fig. 1, for a rather large range of C-Ni layer separations (or, equivalently, C-Ni nearest-neighbor distances). A summary of results for the four geometries we have considered, each at the optimal layer separation, is presented in Table 1. In order to have a common reference, the total energy results are expressed as interface formation energies, i.e., the energies of the interfaces with respect to the two isolated bulk phases.

Table 1. Theoretical interface formation energies and Schottky-barrier heights (SBH) for the four diamond/Ni interfaces geometries discussed in the text, each at the calculated equilibrium diamond-Ni layer separation.

Interface plane and orientation		Formation energy (eV/atom)	SBH(eV)
(111) in-hollow (T ₄)		1.06	0.8
(111) tetrahedral (atop)		0.97	< 0.1
(100) in-hollow (4-fold)		1.92	1.0
(100) tetrahedral (bridge)		1.03	< 0.1

The most striking feature of the results in Table 1 is the *essential disappearance of the Schottky barrier for the tetrahedral orientations* of both the (111) and (100) interfaces. This degree of sensitivity of the SBH to interface orientation is, to our knowledge, without experimental or theoretical precedent. In order to account for it, we examine in some detail the relationship between barrier height and chemical bonding across the interface. This can be addressed in several ways; we begin with the formation energy results of Table 1. First, from Fig. 1, it is clear that all the geometries considered are stable with respect to the free surfaces, and in fact are relatively strongly bonded. Although all four geometries show positive formation energies (thermodynamic instability with respect to disproportionation into the bulk phases), this is generally true of such calculations, especially in light of the very high cohesive energy of bulk diamond. Note that in both the (111) and (100) interfaces, the tetrahedral orientation is energetically preferred. Second, for both interfaces, the tetrahedral orientation leads to an equilibrium C-Ni bond length roughly 10 percent shorter than for the in-hollow. Together, these two observations suggest a picture in which

the tetrahedral orientations lower their energy through the formation of stronger (partly covalent) bonds, and in which the in-hollow orientations achieve stability through some weaker bonding mechanism.

In Fig. 2 we plot the difference density,

$$\Delta\rho(r) = \rho_{SCF}(r) - \rho_{OAC}(r), \quad (2)$$

for the (111) interface in the in-hollow and tetrahedral orientations; here $\rho_{SCF}(r)$ is the self-consistent valence charge density, and $\rho_{OAC}(r)$ is constructed from overlapping atomic charge densities. Common to both plots are the large charge accumulations between carbon atoms along a bonding chain. These are the purely covalent sp^3 bonds characteristic of cubic bulk diamond. Also evident in both plots are the metallic-like charge rearrangements in the nickel slab, in which charge moves into the interstitial regions. At the interface plane, however, the behavior in the two orientations is quite distinct. The charge excess in the tetrahedral orientation, Fig. 2(a), is centered on the C-Ni interatomic axis with a maximum value $0.14e/\text{\AA}^3$, twice as large as found in the interstitial region, and so may be described as a bond of primarily covalent character. For the in-hollow orientation, Fig. 2(b), the interface region shows a charge distribution whose magnitude and position (with

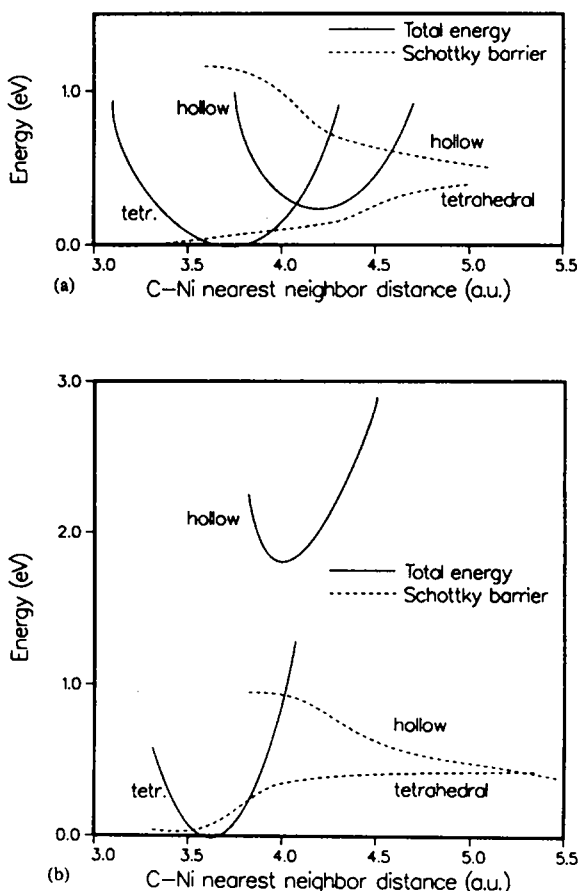


Fig. 1. Theoretical total energies and Schottky-barrier heights (SBH) for the (a) diamond/Ni(111) and (b) (100) interfaces, in the tetrahedral (atop and bridge) and in-hollow (T₄ and 4-fold) orientations.

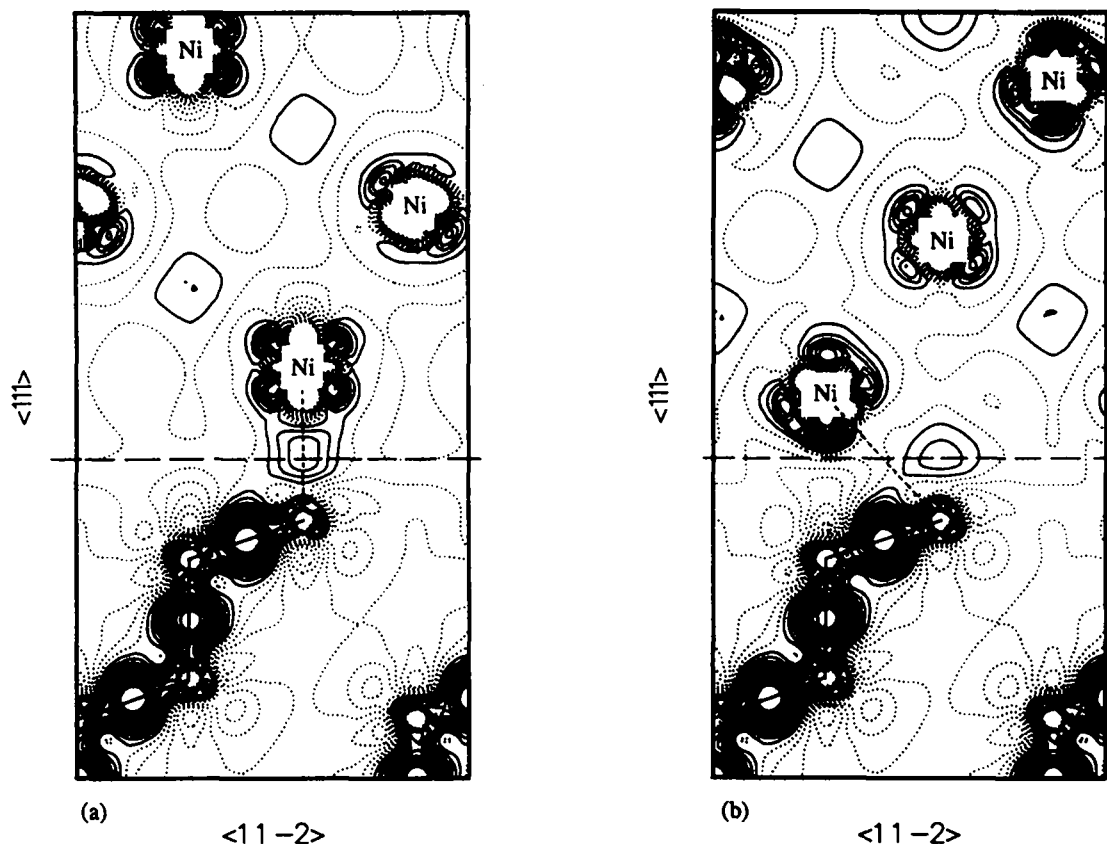


Fig. 2. Charge-density differences for the diamond/Ni(111) interface in (a) the tetrahedral orientation, and (b) the in-hollow orientation. Solid (dotted) curves represent charge surplus (deficit). Heavy solid lines indicate diamond bonding chains, dashed lines mark the interface plane, and straight dotted lines mark the C-Ni internuclear axes.

respect to the Ni surface) are nearly identical to bulk Ni interstitial density. In contrast to the tetrahedral orientation, this distribution clearly shows no tendency for (covalently) aligning *toward* the surface Ni atoms, although these Ni atoms themselves partially polarize in the direction of the charge maximum. Neither case bears much resemblance to the free diamond surface, for which the density difference in the same region is less than $10^{-2}e/\text{\AA}^3$, and so neither distribution can be attributed solely to dangling carbon bonds. Of course, the magnitude of the tetrahedral-orientation charge accumulation is still substantially less than the charge-difference maximum along a diamond bonding chain. Nonetheless, on the basis of (i) the formation-energy results, (ii) the equilibrium C-Ni interatomic distances, and (iii) the relative charge density distributions, it is apparent that the tetrahedral orientation leads to a partially formed bond of primarily covalent character, and that the in-hollow orientation results in weaker, non-covalent bonding, accompanied by a frustrated dangling bond. The same analysis holds for the two orientations of the (100) interface, and the corresponding conclusions apply.

The nature of the available interface states not only determines the type of chemical bonding that occurs, but also governs the formation and height of the Schottky barrier. In

Fig. 3(a) we show a portion of the band structure for the clean, unreconstructed diamond (111) surface. The single dangling bond gives rise to a rather flat surface state; partial occupation of this state fixes the Fermi level at 1.0 eV above the VB maximum. In Figs. 3(b) and 3(c) we show the corresponding band structure for the diamond/Ni(111) interface in the tetrahedral and in-hollow orientations, respectively. The dangling bond orbitals of the surface C atoms mix strongly with Ni 3d states near E_F , producing two interface-state bands: a lower C-like band and an upper Ni-like band (denoted by X's and O's, respectively). (Each band has two branches, arising from the two interfaces per unit cell. The splitting of the Ni-band, of order 0.5 eV or less, is largely confined to energies above E_F , and so does not affect the ground state appreciably.) For both orientations, the Fermi level sits at a point 0.7 eV below the top of the C-like band (at K). A similar mechanism, in which E_F is pinned at the average energy of the dangling-bond, has been discussed by Lefebvre *et al* [15]. In the present study, the combination of Fermi-level pinning by the C-like band, and the energy dependence (relative to E_V) of this band on interface orientation, results in large variations in the SBH. In particular, the stronger bonding found in tetrahedral orientations lowers E_F almost to the top of the

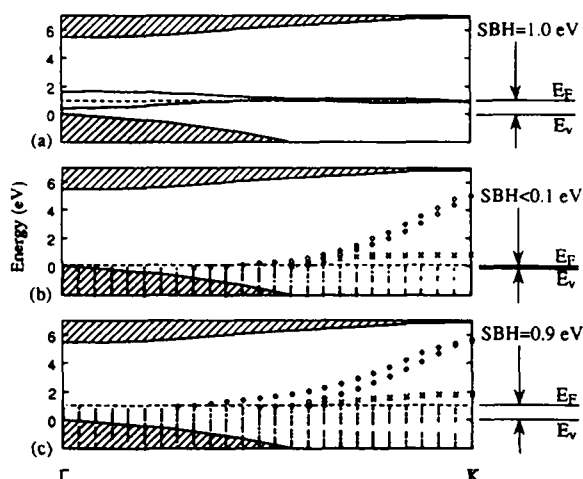


Fig. 3. Two-dimensional band structures for (a) the clean diamond(111) surface, and the diamond/Ni(111) interface in the (b) tetrahedral, and (c) in-hollow interface. For each panel, the energy zero is the bulk diamond VB maximum, and a dashed line marks the Fermi level. C-like and Ni-like bands are denoted by X's and O's, respectively. The projected bulk valence and conduction bands are also shown.

VB, and thereby produces ohmic contacts.

Finally, we emphasize that diamond Schottky-barrier suppression is not unique to interfaces with Ni. We have found identical results for diamond/Cu and diamond/Al interfaces, and are presently extending these studies to other metals. The arguments we have proposed may apply generally to any 1×1 interface of a covalent semiconductor with a normal metal, and, with modifications, to ordered interfaces with more complex surface unit cells. Indeed, the present results have particular relevance for inhomogeneous Schottky barriers [16], for which the experimentally observed SBH is a weighted average based on "local

SBH's"; for non-epitaxial interfaces, a small patch of interface will contain a wide range of orientations, and consequently (as in the present case) a large range of values of local SBH's. It remains to be seen whether such phenomena can be detected experimentally in real interfaces.

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